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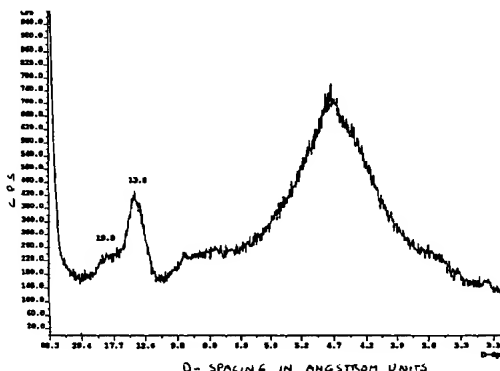
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(54) Title: ORGANOCLAY COMPOSITIONS PREPARED FROM ESTER QUATS AND COMPOSITES BASED ON THE COMPOSITIONS



(57) Abstract: Organoclays based on specific types of ester quats may be remarkably effective for use in preparing nanocomposites. These organoclays may comprise the reaction product of a smectite clay and a quaternary ammonium compound (or "quat") which may comprise two esterified radicals (hereinafter called a "diester quat"). The diester quat may be present in admixture with further quaternary ammonium compounds having esterified radicals, especially compounds having three esterified radicals (hereinafter "triester quats"); or compounds having a single esterified radical (hereinafter "monoester quats"). Where such a mixture of quats is used, the reaction is between the smectite clay and the quat mixture. The diester quat may be present at greater than 55 wt.% of the quaternary mixture; and any triester quat may be less than 25 wt.%, with the fatty acids corresponding to the esters in the mixture having a degree of unsaturation such that the iodine value may be from about 20 to about 90.

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**TITLE: ORGANOCLAY COMPOSITIONS PREPARED FROM ESTER QUATS AND COMPOSITES
BASED ON THE COMPOSITIONS**

FIELD OF THE INVENTION

This invention relates generally to organophilic clays (hereinafter referred to as "organoclays"), and more specifically relates to organoclays prepared from smectite clays which have been treated with a quaternary ammonium compound. The resultant organoclays may be useful as functional additives for organic based systems, where they may confer desired mechanical or physical properties sought for such systems.

BACKGROUND OF THE INVENTION

Organoclays represent the reaction product of a smectite-type clay with a higher alkyl containing ammonium compound (often a quaternary), and have long been known for use in gelling of organic liquids such as lubricating oils, linseed oil, toluene and the like and for use as rheological additives in a variety of organic based liquid systems and solvents. The general procedures and chemical reactions pursuant to which these organoclays are prepared are well known. Thus under appropriate conditions the organic compound which includes a cation may react by ion exchange with clays which include a negative layer lattice and exchangeable cations to form the organoclay products. If the organic cation includes at least one alkyl group including at least ten carbon atoms then the resultant organoclays may have the property of swelling in certain organic liquids. Among the further prior art patents which discuss at length aspects of the preparation and properties of organoclays are U.S. Patents Nos. 2,531,427, 2,966,506, 3,974,125, 3,537,994, and 4,081,496.

As utilized in the present specification, the term "smectite" or "smectite-type clays" refers to the general class of clay minerals with expanding crystal lattices, with the exception of vermiculite. This may include the dioctahedral smectites comprising montmorillonite, beidellite, and nontronite, and the trioctahedral smectites, comprising saponite, hectorite, and sauconite. Also included may be smectite-clays prepared synthetically, e.g. by hydrothermal processes as disclosed in U.S. Patents Nos. 3,252,757; 3,586,468; 3,666,407; 3,671,190; 3,844,978; 3,844,979; 3,852,405; and 3,855,147.

In addition to their functions as thixotropes, organoclays may find numerous other applications. Of particular interest may be composite materials composed of an organic polymer and a smectite-type clay mineral, wherein the mineral may be connected to the polymer through ionic or other bonding. Prior art pertinent to such composites include U.S. Patent No. 2,531,3963, published November 28, 1950, wherein a reinforced elastomer is disclosed. Smectite clays such as bentonite and hectorite may be base exchanged with organic amines or salts thereof such as triethanolamine hydrochloride. Quaternary ammonium compounds may also be used. The resulting compounds, which are therefore "organoclays", may be added to the lattices of elastomers. The organoclays may be added to the latex of any elastomer including natural rubber, and a large list of polymers and/or copolymers is provided. The resulting compositions may be vulcanized.

Japan Laid Open Application S51(76)-109998, deriving from application SHO 50(1975)-3580 was published Sept 29, 1976, and is entitled "Method for Manufacturing a Clay-Polyamide Composite". It discloses a method for manufacturing a clay-polyamide composite characterized by carrying out the polymerization of lactam in the presence of a clay-organic compound composite made by carrying out ion exchange to bond an organic compound which

includes at least one amino group and has the catalyst effect of polymerizing the lactam and clay. The organic compounds mentioned include ω -aminocaproic acid, a nylon salt, hexamethylenediamine, and aminodecanoic acid. The lactams include ϵ -caprolactam and others such as ω -enantholactam, ω -capryllactam, and ω -lauro lactam. The clays used include the montmorillonite group of clay minerals such as montmorillonite, hectorite, etc; and other clays are listed. Montmorillonite is preferred because of the high exchange capacity. The composite is made by first ion exchanging the clay with the organic compound under aqueous conditions, after which the suspension is washed, filtered and dried, then crushed. The organoclay and lactam are mixed, with the organoclay being 10 to 75 wt% of the mixture. During mixing the mixture is brought to 80-100° C to melt the lactam. Polymerization is carried out at 240° C to 260° C. In the resulting composite product it is stated that the silicate layer has a thickness of 9.6 Angstroms. In a first example the interlayer distance of the organoclay layers before polymerization was 3.4 Angstroms, and 13.1 Angstroms after polymerization. In Example 4 the interlayer distance was 6.5 Angstroms before polymerization, and 50.6 Angstroms after polymerization. The composite produced is stated to have good fire-retardant properties, and improved mechanical properties.

Similarly, in Kawasumi *et al.*, U.S. Patent No. 4,810,734 a process is disclosed wherein a smectite-type clay mineral is contacted with a swelling agent in the presence of a dispersion medium thereby forming a complex. The complex including the dispersion medium is mixed with a monomer, and the monomer is then polymerized. The patent states that the swelling agent acts to expand the interlayer distance of the clay mineral, thereby permitting the clay mineral to take monomers into the interlayer space. The swelling agent is a compound having an onium ion and a functional ion capable of reacting and bonding with a polymer compound. Among the polymers utilizable are polyamide resins, vinyl polymers, thermosetting resins, polyester resins, polyamide resins and the like. Related disclosures are found in U.S. Patents Nos. 4,739,007 and 4,889,885.

In recent years the clay-polymer composite materials above discussed have been referred to as nanocomposites, a term which reflects their property of exhibiting ultrafine phase dimensions, typically in the range 1-100nm. The number of nanocomposites based on smectite-type clays and linear thermoplastics is growing. Wang and Pinnavaia, *e.g.*, have reported delamination of an organically modified smectite in an epoxy resin by heating an onium ion exchanged form of montmorillonite with epoxy resin to temperatures of 200-300°C. Chemistry of Materials, vol. 6, pages 468-474 (April, 1994). Similarly in United States Patent No. 5,554,670 an epoxy-silicate nanocomposite is disclosed which is prepared by dispersing an organically modified smectite-type clay in an epoxy resin together with diglycidyl ether of bisphenol-A (DGEBA), and curing in the presence of either nadic methyl anhydride (NMA), and/or benzyldimethyl amine (BDMA), and/or boron trifluoride monoethylamine (BTFA) at 100-200°C. Molecular dispersion of the layered silicate within the crosslinked epoxy matrix is obtained, with smectite layer spacings of 100Å or more and good wetting of the silicate surface by the epoxy matrix. Additional recent references evidencing the increasing interest in nanocomposites incorporating organoclays in polymer matrices include United States Patents Nos. 5,164,440; 5,385,776; 5,552,469; and 5,578,672.

Thus in a typical procedure for preparing a nanocomposite, the smectite clay, most commonly a montmorillonite, may be treated with an organic ammonium ion to intercalate the organic molecule between the silicate layers of the clay, thereby substantially swelling or expanding the interlayer spacing of the smectite. (The reaction product resulting from this treatment may in accordance with the foregoing discussion, be referred to herein as an "organoclay"). Thereafter the expanded silicate layers may be separated or exfoliated in the presence of or with the

assistance of a polymer with which groups on the intercalated organic molecule may be compatible. A monomer may also be used which may be polymerized after being intermixed with the intercalated clay.

SUMMARY OF THE INVENTION

In one embodiment organoclays may include the reaction product of a smectite clay and a quaternary ammonium compound (hereinafter simply "quat") which may include two esterified radicals (hereinafter called a "diester quat"). The diester quat may be present in admixture with further quaternary ammonium compounds having esterified radicals, especially compounds including three esterified radicals (hereinafter "triester quats"); or compounds including a single esterified radical (hereinafter "monoester quats"). Where such a mixture of quats may be used, the reaction may be between the smectite clay and the quat mixture. The diester quat may be present as greater than 55 wt% of the quaternary mixture; and the triester quat may be less than 25 wt%, with the fatty acids corresponding to the esters in the mixture having a degree of unsaturation such that the iodine value is from about 20 to about 90. More preferably in such a mixture the diester quat content may be greater than 60 wt%, the triester quat content may be less than 20 wt%, and the iodine value may be from about 30 to about 70. Yet more preferably the diester quat content may be greater than 62%, the triester quat content may be less than 17 wt%, and the iodine value may be from about 40 to about 60, and more optimally from about 45 to about 58.

BRIEF DESCRIPTION OF DRAWINGS

In the drawings appended hereto:

FIGURE 1 is a wide angle X-ray scan pattern for an organoclay in accordance with the present invention;

FIGURE 2 is a wide angle X-ray scan pattern for a clay-polymer nanocomposite prepared using the organoclay depicted in Figure 1;

FIGURE 3 is a wide angle X-ray scan pattern for a prior art ester quat-based organoclay;

FIGURE 4 is a wide angle X-ray scan pattern for a clay-polymer nanocomposite prepared using the organoclay the scan for which is depicted in Figure 2;

FIGURE 5 is a wide angle X-ray scan pattern for a prior art quat-based organoclay, where the quat does not include esterified radicals; and

FIGURE 6 is a wide angle X-ray scan pattern for a clay-polymer nanocomposite prepared using the organoclay the scan for which is depicted in Figure 5.

DETAILED DESCRIPTION OF THE INVENTION

The quaternary ammonium compounds which may be reacted with the smectite clays to produce the organoclays of the present invention may be high in diester and low in triester content. They may be obtained by reaction of C_{12} - C_{22} fatty acids or the hydrogenation products thereof, or a mixture of such acids, with an alkanolamine in the presence of an acid catalyst, wherein the ratio of fatty acid to alkanolamine may be from about 1.40 to 2.0. The resultant ester amine reaction products may be subsequently quaternized to obtain quaternary ammonium salts for reaction with the smectite. The fatty acid may be a C_{16} - C_{22} acid include a degree of unsaturation such that the iodine value is in the range of from about 3-90, preferably, from about 20-90, more preferably in the range of 40-60 and still more preferably in a range of from about 45-55. Preferred fatty acids may include but are not limited to oleic, palmitic,

erucic, eicosanic, and mixtures thereof. Soy, tallow, palm, palm kernel, rape seed, lard, mixtures thereof and the like may be typical sources for fatty acid which may be employed in this aspect of the invention.

It may be also preferred that the fatty acid(s) employed in the present process may have a cis to trans isomer ratio of from about 80:20 to about 95:5. More preferably, the trans isomer content of said fatty acid(s) may be less than about 10%. An optimum trans-isomer content may be between about 0.5 - 9.9%. The most preferred fatty acid may be a mixture of tallow/distilled tallow having a cis:trans isomer ratio of greater than 9:1.

The alkanolamines employable in the present invention generally correspond to the general formula:



wherein R, R₁ and R₂ may be independently selected from C₁ - C₆ hydroxyalkyl groups. Preferred alkanolamines may include but are not limited to triethanolamine, propanol diethanolamine, ethanol diisopropanolamine, triisopropanol amine, diethanolisopropanol amine, diethanolisobutanolamine and mixtures thereof.

The molar ratio of fatty acid to alkanol amine may be generally in the range of from about 1.4 to 2.0, preferably from about 1.55 - 1.90, and more preferably, in the range of from about 1.65-1.75. Best results may be obtained when the molar ratio is between about 1.68-1.72. The acid catalyst employable in the present process may include, but is not limited to, acid catalysts such as sulphonic acid, phosphorous acid, p-toluene sulphonic acid, methane sulphonic acid, oxalic acid, hypophosphorous acid or an acceptable Lewis acid in an amount of 500-3000 ppm based on the amount of fatty acid charge. A preferred acid catalyst may be hypophosphorous acid. Typically, 0.02 - 0.2 % by weight, and more preferably 0.1 to 0.15 % by weight of acid catalyst, based on the weight of fatty acid, may be employed in the present process.

The esterification of fatty acids with alkanolamines may be carried out at a temperature of from about 170° - 250°C until the reaction product has an acid value of below 5. After the esterification, the crude product may be reacted with alkylating agents in order to obtain the quaternary ammonium product. Preferred alkylating agents may include C₁ - C₄ straight or branched chain alkyl halides, phosphates, carbonates, or sulfates, C₇ - C₁₀ arylalkyl halides, phosphates or sulfates, and mixtures thereof. Examples of preferred alkylating agents may include but are not limited to methyl chloride, benzyl chloride, diethyl sulfate, dimethyl carbonate, trimethyl phosphate, dimethyl sulfate or mixtures thereof. Choosing the type and amount of alkylating agent employed is well within the skill of one in the art. Typically, when dimethyl sulfate is the alkylating agent, 0.7 to 1.0, preferably 0.75 to 0.98 mol dimethyl sulfate per mole of esteramine may be satisfactory in yielding the quaternized product.

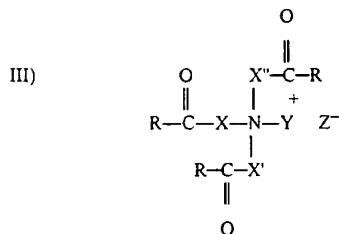
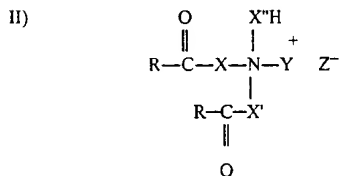
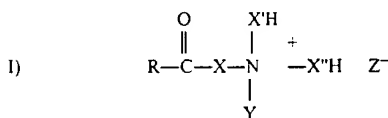
In one embodiment, dimethyl sulfate, a strong alkylating agent, may be employed because of the long reaction times encountered when weaker alkylating agents, such as methyl chloride, are employed. The quaternization reaction time may also be reduced, in many cases by 50% or more, if the esteramine mixture to be quaternized includes minimal amounts of triester component. By modifying esterification conditions, the amount of triesteramine component formed in the esteramine mixture may be minimized. Reducing the amount of triester component, by even a relatively small amount, may lead to a significant reduction in quaternization reaction time. This allows one to utilize weaker alkylating agents, such as methyl chloride, which may be less expensive and less toxic, without the disadvantage of excessively

long reaction times. Further, the performance of the final product may not be impaired and, in fact, an improvement in performance may be typical. Similar improvements with other alkylating agents have been observed.

Triester formation in the esteramine mixture may be minimized by accelerating the heat up rate in the esterification reaction of fatty acids with alkanolamines. In one embodiment, an accelerated heat up rate of greater than about 0.4°C/minute, more preferably greater than about 0.8°C/minute, and still more preferably greater than about 1.25 C/minute, from a temperature of about 70°C to a temperature in a range of from between 170°C to 250°C may be effective in minimizing triester formation in the ester amine mixture.

The quaternization may be carried out in bulk or in solvent, at temperatures ranging from 60° - 120° C. If a solvent is employed, then the starting materials and/or product should be soluble in the solvent to the extent necessary for the reaction. Solvents of this type are generally known in the art. Suitable examples may include polar solvents such as, for example, lower alcohols, i.e., C₁ - C₆ alcohols. Other solvents which may be employed include, but are not limited to mono-, di-, and tri-glycerides, fatty acids, glycols and mixtures thereof.

The preferred quaternary ammonium salt for the invention comprises a mixture of mono - (I), di- (II) and triester (III) components of the following formulae:



wherein X, X' and X'' may be the same or different and may be selected from straight or branched chain, optionally substituted oxyalkylene or polyoxyalkylene groups having from 2-6 carbon atoms, preferably 3-6 carbon atoms, where the oxyalkylene units number from about 1-10, preferably 1-5, and still more preferably 1-2; each R group may be individually selected from straight or branched chain, optionally substituted alkyl groups having from 11 to 23 carbon

atoms. Y may be an alkylphenyl group or a straight or branched chain optionally substituted C_1 to C_6 alkyl or alkylene group; and Z' represents a softener compatible anion including but not limited to halogen, CH_3SO_4 or $C_2H_5SO_4$.

The reaction products may also include minor amounts of methyl trialkanolammonium salts and other impurities. The amount of diester in the final product (II) may be generally greater than about 55% by weight and the amount of triester (III), based on the gas chromatograph of the ester amine, may be generally less than about 25%, preferably less than 20% by weight based on the total amount of quaternary ammonium salt product.

Typical product compositions may include an ester distribution within the following ranges: greater than about 55 wt% diester and less than about 25 wt% triester, with a total fatty acid iodine value of from about 20 to about 90; more preferably, greater than about 60 wt% diester and less than about 20 wt% triester, with a total iodine value of from about 30 to about 70; and still more preferably, greater than about 62 wt% diester and less than about 17 wt% triester, with a total iodine value of from about 40 to about 60. In many instances triester content may be in the 10.0 to 17.0 wt% range. In a most preferred embodiment, the fatty acid iodine value may be between about 45 to about 58.

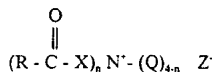
The ratio of cis to trans double bonds of the above salts may be preferably in the range of from about 80:20 to about 95:5. Preferably, the cis:trans ratio may be greater than about 90:10. In a most preferred embodiment, the amount of trans isomer ideally may be in the range of from 5 to 9.5%.

There are several convenient methods for obtaining the desired cis:trans ratio of the quaternary ammonium salt product. The preferred method may be to produce the quaternary ammonium salt from cis-isomeric and trans-isomeric fatty acids after adjusting said acids to the desired ratio.

Another method may be to produce the quaternary ammonium salt from the mixture after adjusting the ratio thereof by isomerizing a portion of the cis-isomeric fatty acid or ester thereof into the trans-isomer, in the presence of a metallic catalyst. Other methods may be readily apparent to and well within the skill of one of ordinary skill in the art.

The quaternary ammonium compounds according to the present invention may be prepared by reacting at least one C_{12} - C_{22} fatty acid having a iodine value of from 20-90 with an alkanol amine in the presence of an acid catalyst. The ratio of acid to amine may be preferably in the range of 1.4 to 2.0, and the reaction may be carried out at a temperature of from about 170°C to about 250°C until the reaction product has an acid value of below about 5. A heat up rate of at least about 0.8°C per minute may be employed in order to minimize triester formation. The esterification products may be subsequently alkylated in order to obtain the quaternary ammonium product.

In another embodiment, the present invention contemplates a family of quaternary ammonium esters which may be derived from ether alkanolamines. Said quaternary ammonium esters are of the general formula:



where n is an integer of 1 or 2. R is a C_3 to C_{23} straight or branched chain, optionally substituted alkyl group, each X may be the same or different and may be selected from straight or branched chain, optionally substituted oxyalkylene or polyoxyalkylene groups having from 2-6 carbon atoms; each Q may be the same or different and may be selected from a oxyalkylene or polyoxyalkylene group, or a straight or branched chain, optionally substituted alkyl, alkylene, alkylphenyl, hydroxyalkyl, hydroxyalkylene, wherein at least one of said Q groups may be a C_2 to C_6 linear or branched chain oxyalkylene or polyoxyalkylene capped with a C_1 to C_6 alkyl, or an alkyl phenyl group; and Z' is a compatible anion.

The above ester quat may be prepared by reacting a fatty acid and/or fatty acid methyl ester as previously defined herein with an ether alkanolamine. The reaction may be essentially the same as the reaction of said acid and/or said acid ester with an alkanolamine previously described herein, with an exception that the employment of a minimum heat up rate in order to achieve a high diester, low triester containing product may not be necessary. More particularly, the reaction of fatty acid or fatty acid methyl ester with an ether alkanolamine may produce only mono- and di-substituted ester products. This is because the ether group may be non-reactive and may not lead to the formation of a tri-substituted species. Accordingly, the heat up rate which may be an important requirement of the trialkanolamine based process may be less important when ether alkanolamines are employed as a reactant since the formation of tri-substituted species may not be possible.

Further, employment of ether alkanolamines may be beneficial in that they may be more reactive with a broader range of alkylating agents, and the final products may be easier to formulate and may be more storage stable. Finally, the ratio of mono- and di-substituted species may be controlled by controlling the ratio of fatty acid/fatty acid methyl ester to ether alkanolamine.

An exemplary process for the preparation of a high diester quaternary ammonium mixture comprises reacting:

- I) a $C_{11} - C_{23}$ substituted or unsubstituted fatty acid or mixture of fatty acids having an Iodine Value of from about 20 to about 90, and having less than about 20% trans double bonds, with
- II) an ether alkanolamine of the formula:



wherein R may be a $C_2 - C_6$ alkyl ether, and each of R_1 and R_2 may be independently selected from $C_2 - C_6$ hydroxyalkyl groups, wherein the molar ratio of said fatty acid to ether alkanol amine may be from about 1.4 to about 2.0, preferably from about 1.6-1.9, and quaternizing the resultant ester amine mixture in order to obtain an improved high diester quaternary ammonium mixture.

Preferred ether alkanolamines may be methoxyethyldiethanolamine, methoxypropyldiethanolamine, methoxybutyldiethanolamine or mixtures thereof. The high diester quaternary ammonium mixture derived from ether alkanolamines in accordance with the present invention generally may have a diester content of at least 70 wt%, preferably greater than about 75 wt%, and still more preferably, greater than about 80 wt% on a 100 wt% active basis.

The compositions of the present invention having high diester content and low triester content demonstrate superior performance particularly in preparation of nanocomposites as compared to typical ester amine quaternary compounds.

Preferably, the smectite may be a natural or synthetic clay mineral such as hectorite, montmorillonite, bentonite, beidelite, saponite, stevensite or mixtures thereof. A particularly preferred choice of the smectite is hectorite.

In a preferable procedure for preparing the organoclay composition, the smectite mineral, such as hectorite, may be crushed, ground, slurried in water and screened to remove grit and other impurities. The smectite may be preferably converted to the sodium form if it is not already in this form. This may be effected, as is known in the art, by a cation exchange reaction, or the clay may be converted via an aqueous reaction with a soluble sodium

compound. The smectite mineral may then be subjected as a dilute (1 to 6% solids) aqueous slurry to high shearing in a suitable mill. Most preferred for use in this shearing step may be a homogenizing mill of the type wherein high speed fluid shear of the slurry may be effected by passing the slurry at high velocities through a narrow gap, across which a high pressure differential is maintained. This type of action may e.g. be effected in the well-known Manton-Gaulin "MG") mill, which device is sometimes referred to as the "Gaulin homogenizer". Reference may be made to U.S. patents Nos. 4,664,842 and 5,110,501 (assigned to the assignee Southern Clay Products Inc.) for further details of such mill. The conditions for use of the MG mill may be substantially as in the said patents; e.g. the said pressure differential across the gap is preferably in the range of from 70,300 to 562,400 g/cm² with 140,600 to 351,550 g/cm² being more typical in representative operations. Depending upon the specifics of the equipment, pressures higher than 562,400 g/cm² may be readily used. The slurry to be treated may be passed one or more times through the MG mill. Among additional instrumentalities which may be effectively utilized in the present invention to provide high shearing of the clay component, may be the rotor and stator arrangement described in the assignee Southern Clay Products' U.S. Patent No. 5,160,454. Following the high shear step, the slurry may be intermixed with the quaternary ammonium salt and the reaction slurry may be preferably again subjected to high shearing by one or more passes through the MG or other mentioned instrumentalities. The slurry may thereupon be dewatered, and the quaternary ammonium-treated clay dried and ground to provide a dry organoclay product.

When used in composites such as nanocomposites, the organoclay compositions of the invention may yield unexpected improvements in the mechanical and other properties of the composite, including with respect to tensile strength, tensile modulus and flex modulus, all of which may be highly significant attributes for the plastics and similar formulations.

The organoclays of the invention may be used in preparing nanocomposites by any of the methods which are set forth in the prior referenced patents, and with a large variety of polymerizable resins such as polyamides, epoxy, polyvinyl, polyacrylamide, etc.

The invention will now be illustrated by examples, which may be regarded as illustrative and not delimitative of the invention. Unless otherwise indicated to the contrary, all parts and percentages are by weight.

Example 1

An organoclay composition in accordance with the invention was prepared from a smectite mineral clay which was processed as above described, i.e. crushed, ground, slurried in water and screened, converted to its sodium form, and then subjected to high shear by being passed as a dilute slurry through an MG mill, and then as a slurry treated with the quaternary ammonium compound in accordance with the invention. This quaternary composition was a diester quat in admixture with further quaternary ammonium compounds having esterified radicals, especially compounds having three esterified radicals (hereinafter "triester quats"); or compounds having a single esterified radical (hereinafter "monoester quats"). The reaction forming the organoclay was between the smectite clay and the quat mixture. The diester quat was present as greater than 55 wt% of the quaternary mixture; and the triester quat was present as less than 25 wt%, with the fatty acids corresponding to the esters in the mixture having a degree of unsaturation such that the iodine value is from about 20 to about 90. A wide angle x-ray scan pattern for the product resulting from the reaction is shown in Figure 1, where the detected reflection intensity in counts/second is plotted against the D-spacing in

Angstrom Units. The 001 reflection peak indicates a remarkably high D_{001} spacing for the organoclay of 59.1 Angstroms, and suggests that the organoclay will exhibit a very high exfoliation efficiency in nanocomposites.

Example 2

Five (5) wt% of the organoclay powder of Example 1 was premixed with high impact polystyrene ("HIPS") pellets by mechanical means. 50 to 60 g of this dry blend was added to a Brabender mixer which was then operated at 60 rpm. The temperature of the mixer was varied from 190°C to 230°C. The time of melt blending in the mixer was varied from 15 minutes to one hour. At the end of the prescribed time, the molten mixture was extruded from the Brabender. The resulting nanocomposite sample was prepared for x-ray analysis by pressing the mixture in a Wabash press with the platens heated to 150°C. at a pressure of 7,500 to 10,000 p.s.i. for one minute. A 1-1/8" by 1-1/8" square was cut from the sample for analysis. The resulting wide angle x-ray scan pattern is shown in Figure 2. The D_{001} reflection peak of the organoclay is completely gone in this composite indicating very high exfoliation of the organoclay in the HIPS matrix.

Example 3

In this Example an organoclay sample was prepared using the procedure of Example 1, except that in this instance the quat used was a diester quat (based on hydrogenated tallow), which in part differs from the quat used in Examples 1 and 2 in including methyl groups on the remaining two -N bonds, whereas the Example 1 quat includes a hydroxyethyl group on one of the said remaining -N bonds. A wide angle x-ray scan pattern for the product resulting from the reaction is shown in Figure 3. The 001 reflection peak indicates a D_{001} spacing for the organoclay of 39.5 Å, which is not as high as the sample of Example 1, although still suggesting that the organoclay will exhibit a reasonably high exfoliation efficiency in nanocomposites.

Example 4

The procedure of Example 2 was used in preparing a nanocomposite, with the organoclay being that prepared in Example 3. The wide angle x-ray scan of this nanocomposite is shown in Figure 4. The D_{001} reflection peak of the organoclay is completely gone in this composite indicating high exfoliation of the organoclay in the HIPS matrix. The peak in the curve marked as 34.2 is probably the 002 reflection. This would indicate an 001d spacing in the exfoliated clay of at least 70 Å.

Example 5

In this Example an organoclay sample was prepared using the procedure of Example 1, except that the quat used was that disclosed for use in preparing the organoclays described in commonly assigned U.S. Patent No. 5,739,087, the contents of which is hereby incorporated by reference. The said quat is a branched chain structure, and is not an ester quat. The corresponding wide angle x-ray appears in Figure 5, from which it is seen that the 001 reflection peak indicates a D_{001} spacing for the organoclay of 19.0 Å, which is nowhere near the as high as the sample of Example 1, and neither as high as the spacing of the sample in Example 3. This indicates that the organoclay will exhibit a considerably lower exfoliation efficiency in nanocomposites.

Example 6

The procedure of Example 2 was used in preparing a nanocomposite, with the organoclay being that prepared in Example 5. The wide angle x-ray scan of this nanocomposite is shown in Figure 6. The 001 reflection peak of the organoclay is seen to appear in the scan of this composite and indicates an spacing of 32.9 Å, which compared especially to the results of Example 2 and to a lesser extent Example 4, indicates a relatively inadequate exfoliation of the organoclay in the HIPS matrix.

While the present invention has been described in terms of specific embodiments thereof, it will be understood in view of the present disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present teaching. Accordingly, the invention is to be broadly construed, and limited only by the scope and spirit of the claims now appended hereto.

WHAT IS CLAIMED IS:

1. An organoclay composition comprising the reaction product of a smectite clay with a quaternary ammonium mixture, the quaternary ammonium mixture comprising a diester quaternary ammonium compound.
2. The composition of claim 1, wherein the quaternary ammonium mixture further comprises triester and/or monoester quaternary ammonium compounds.
3. The composition of claim 2, wherein the diester quaternary ammonium compound is present at greater than 55 wt% of the quaternary ammonium mixture.
4. The composition of claim 1, wherein the diester quaternary ammonium compound is in admixture with a triester quaternary ammonium compound, and wherein the triester quaternary ammonium compound comprises less than 25 wt% of the quaternary ammonium mixture.
5. The composition of claims 1 to 4, wherein fatty acids corresponding to esters in the diester quaternary ammonium compound have a degree of unsaturation such that the fatty acid iodine value is from about 20 to about 90.
6. The composition of claims 4 and 5, wherein the diester quaternary ammonium compound content is greater than 60 wt%, the triester quaternary ammonium compound content is less than 20 wt%, and the fatty acid iodine value is from about 30 to about 70.
7. The composition of claims 4 to 6, wherein the diester quaternary ammonium compound content is greater than 62%, the triester quaternary ammonium compound content is less than 17 wt%, and the fatty acid iodine value is from about 40 to about 60.
8. The composition of claims 6 to 7, wherein the fatty acid iodine value is from about 45 to about 58.
9. The composition of claim 1, wherein the quaternary ammonium compound comprises the reaction product of C_{12} - C_{22} fatty acids or the hydrogenation products thereof, or a mixture of such acids, with an alkanolamine in the presence of an acid catalyst, wherein the ratio of fatty acid to alkanolamine is from about 1.40 to 2.0.
10. The composition of claim 1, wherein the smectite comprises hectorite, montmorillonite, bentonite, beidelite, saponite, stevensite or mixtures thereof.
11. The composition of claim 1, wherein the smectite comprises hectorite.

12. A method of making an organoclay composition comprising reacting a smectite clay with a quaternary ammonium mixture, the quaternary ammonium mixture comprising a diester quaternary ammonium compound.
13. The method of claim 12, wherein the quaternary ammonium mixture further comprises triester and monoester quaternary ammonium compounds.
14. The method of claim 13, wherein the diester quaternary ammonium compound is present at greater than 55 wt% of the quaternary ammonium mixture.
15. The method of claim 12, wherein the diester quaternary ammonium compound is in admixture with a triester quaternary ammonium compound, and wherein the triester quaternary ammonium compound comprises less than 25 wt% of the quaternary ammonium mixture.
16. The method of claims 12 to 15, wherein the fatty acids corresponding to esters in the diester quaternary ammonium compound have a degree of unsaturation such that the fatty acid iodine value is from about 20 to about 90.
17. The method of claim 13, wherein the diester quaternary ammonium compound content is greater than 60 wt%, the triester quaternary ammonium compound content is less than 20 wt%, and the fatty acid iodine value is from about 30 to about 70.
18. The method of claim 13, wherein the diester quaternary ammonium compound content is greater than 62%, the triester quaternary ammonium compound content is less than 17 wt%, and the fatty acid iodine value is from about 40 to about 60.
19. The method of claims 16 to 18, wherein the fatty acid iodine value is from about 45 to about 58.
20. The method of claim 12 to 19, further comprising adding the clay to water to form a slurry.
21. The method of claim 12 to 20, further comprising adding the clay to water to form a slurry wherein the clay is slurried in water up to about 6% by weight of dry clay.
22. The method of claim 12 to 21, further comprising treating the smectite clay with a cation exchange reagent such that the smectite clay is converted to the sodium form of the clay.
23. The method of claim 12 to 22, further comprising treating the smectite clay with a sodium compound such that the smectite clay is converted to the sodium form of the clay.

24. The method of claims 12 and 23, further comprising subjecting the clay to high shear mixing.
25. The method of claims 12 to 23, further comprising subjecting the clay to high shear mixing wherein the high shear mixing is accomplished using a Manton-Gaulin mill.
26. The method of claims 12 to 25, further comprising subjecting the clay to high shear mixing after the clay is reacted with the quaternary ammonium salt.
27. The method of claims 12 to 26, further comprising dewatering and grinding the clay to provide a dry clay product.
28. An organoclay composition made by the method of claims 12 to 27.
29. A composition comprising an organoclay composition as described in claims 1 to 11 and claim 28 and a polymerizable resin.
30. The composition of claim 29, wherein the polymerizable resin is a polyamide.
31. The composition of claim 29 wherein the polymerizable resin is an epoxy.
32. The composition of claim 29 wherein the polymerizable resin is polyvinyl.
33. The composition of claim 29 wherein the polymerizable resin is polyacrylamide.
34. The composition of claim 29 wherein at least 0.1 wt% of the organoclay composition is added to the polymerizable resin
35. A method of forming an article comprising heating a composition as described in claims 29 to 34 and cooling the heated composition.
36. The method of claim 35 wherein heating the composition comprises heating the composition to a melting temperature of the polymerizable resin.
37. The method of claims 35 and 36 wherein heating the composition comprises heating the composition up to about 1 hour.
38. The method of claim 35 wherein heating the composition comprises melt-blending the organoclay with the polymerizable resin.

39. The method of claim 38 wherein heating the composition comprises heating to a temperature sufficient to fluidize the polymerizable resin.

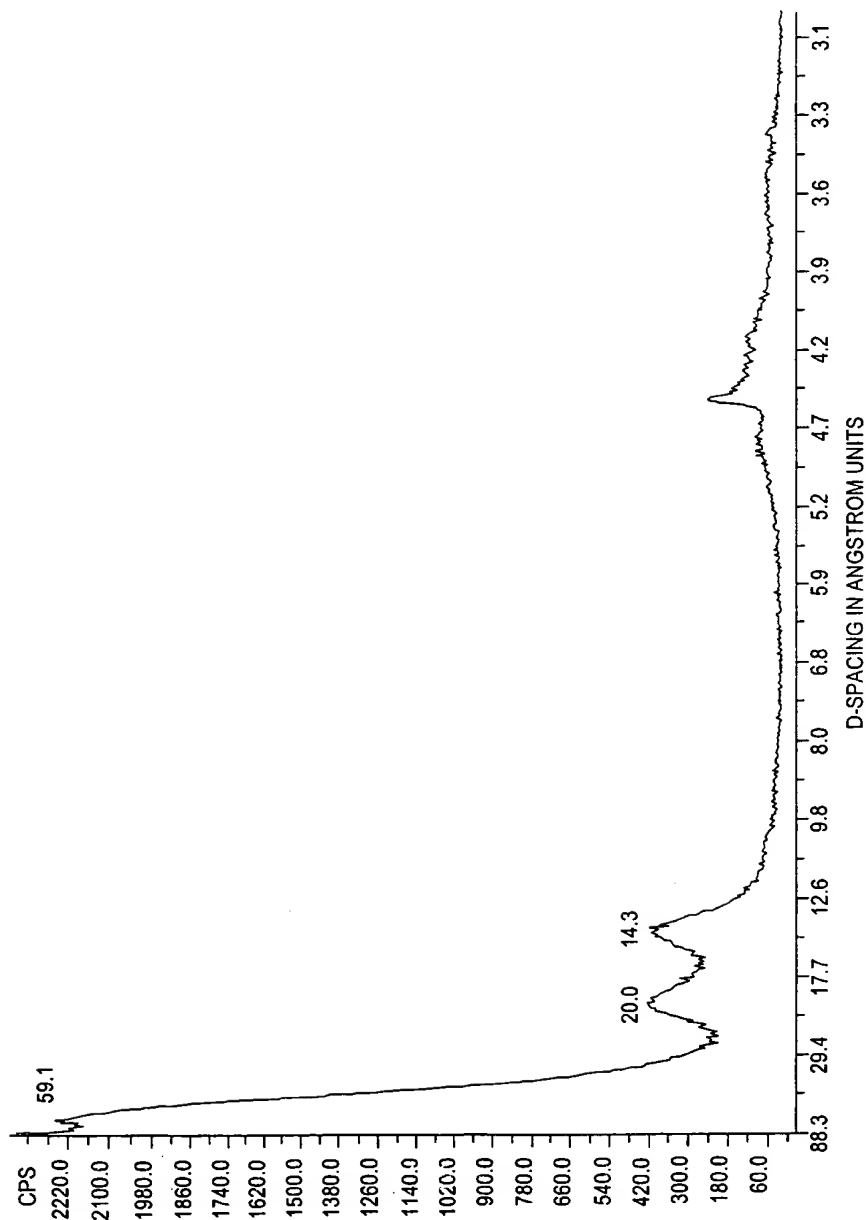
40. The method of claims 35 to 39 wherein cooling the composition comprises extruding the composition through an extruder.

41. An organoclay composition comprising the reaction product of a clay with a quaternary ammonium mixture.

42. A method of making an organoclay composition comprising reacting a clay with a quaternary ammonium mixture.

43. A composition comprising an organoclay composition and a polymerizable resin. .

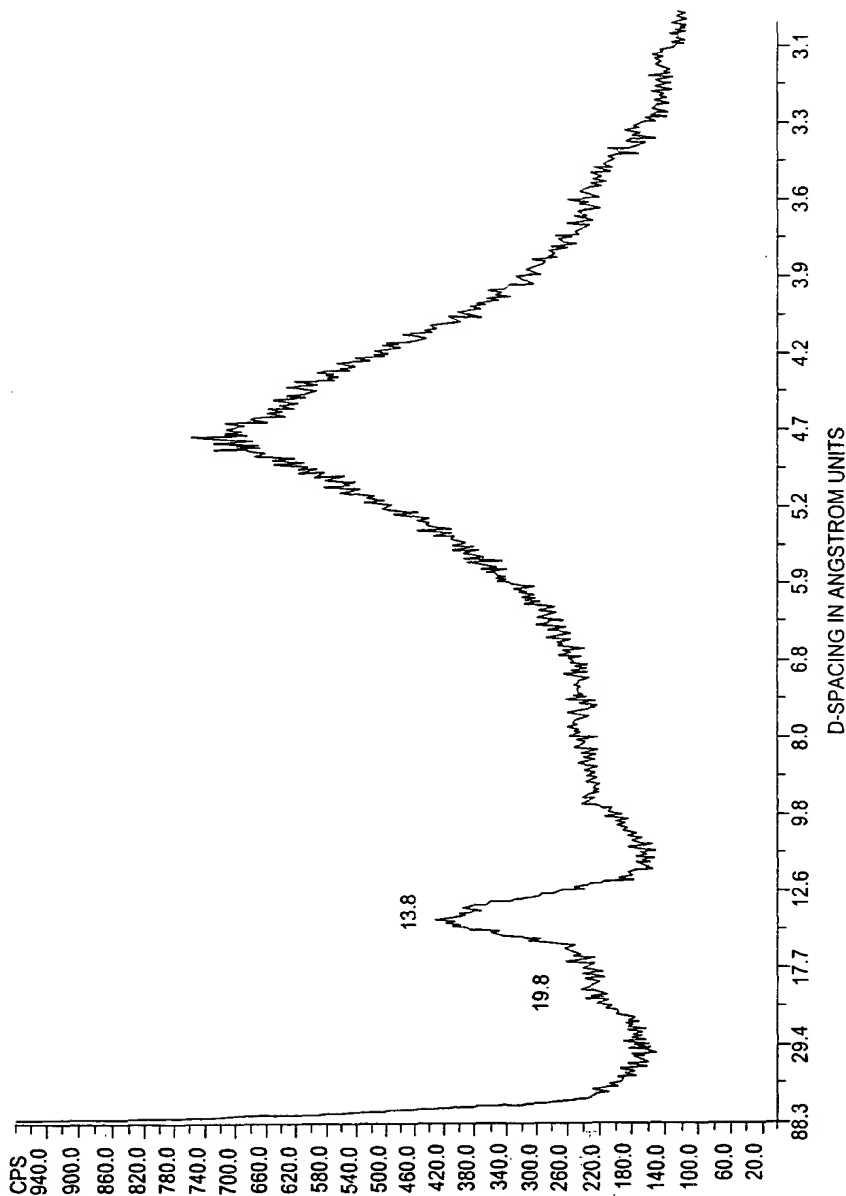
FIG. 1



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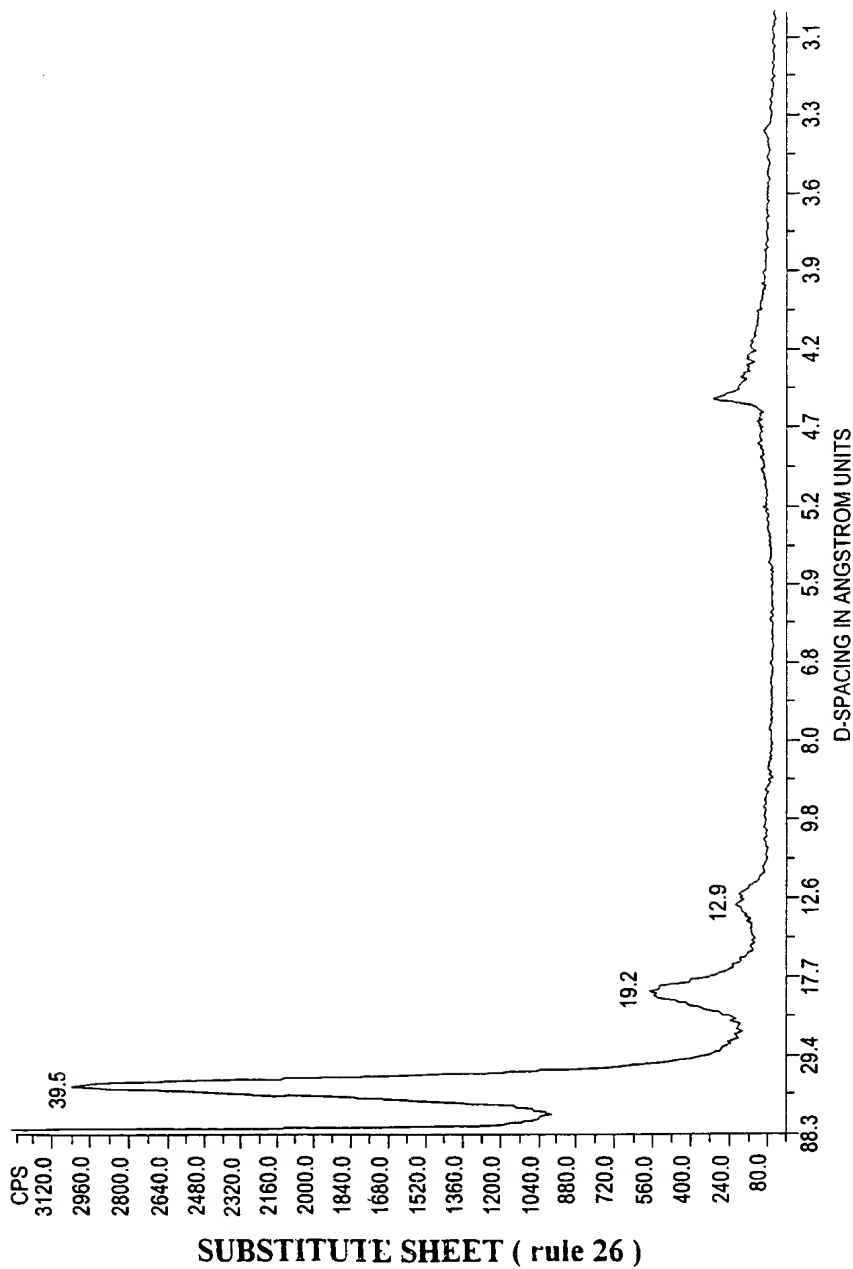
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FIG. 2



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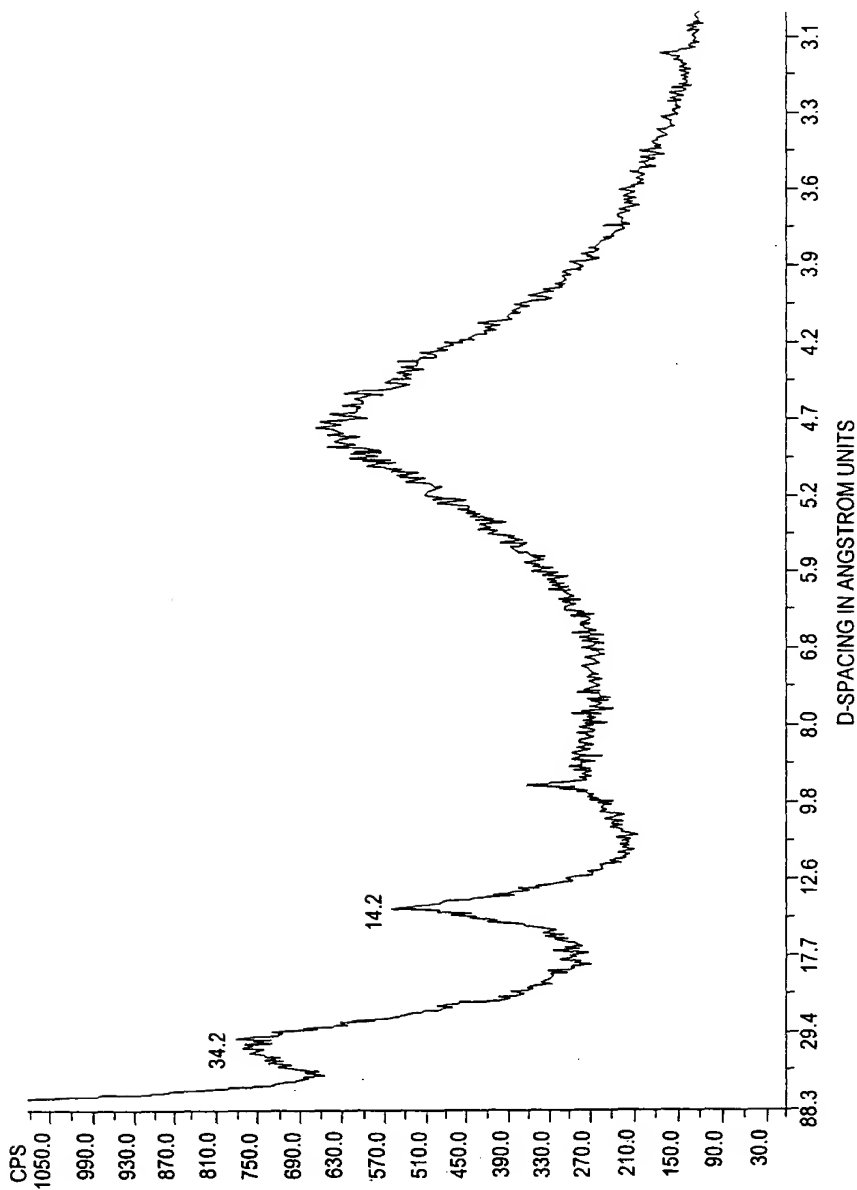
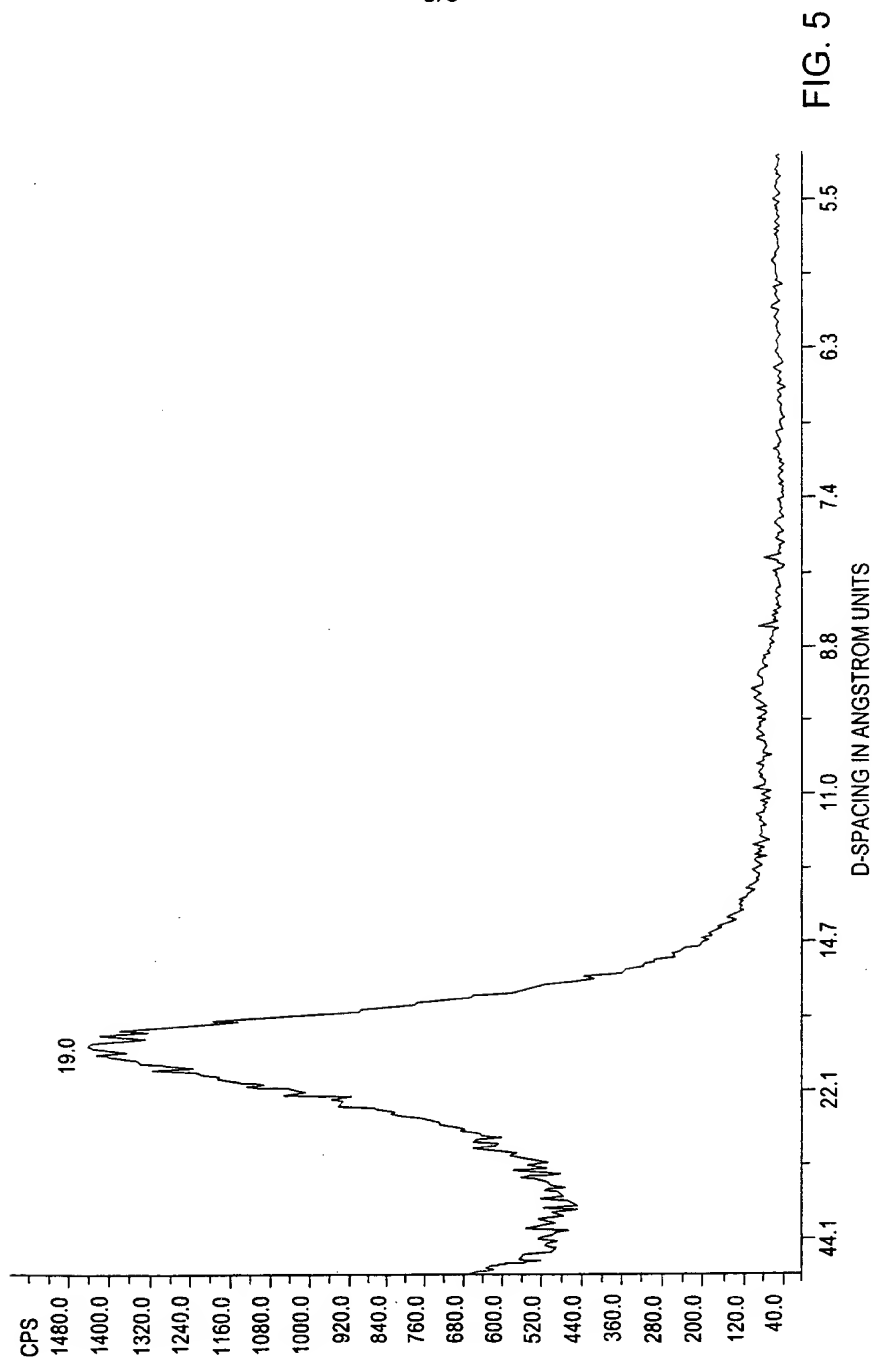


FIG. 4

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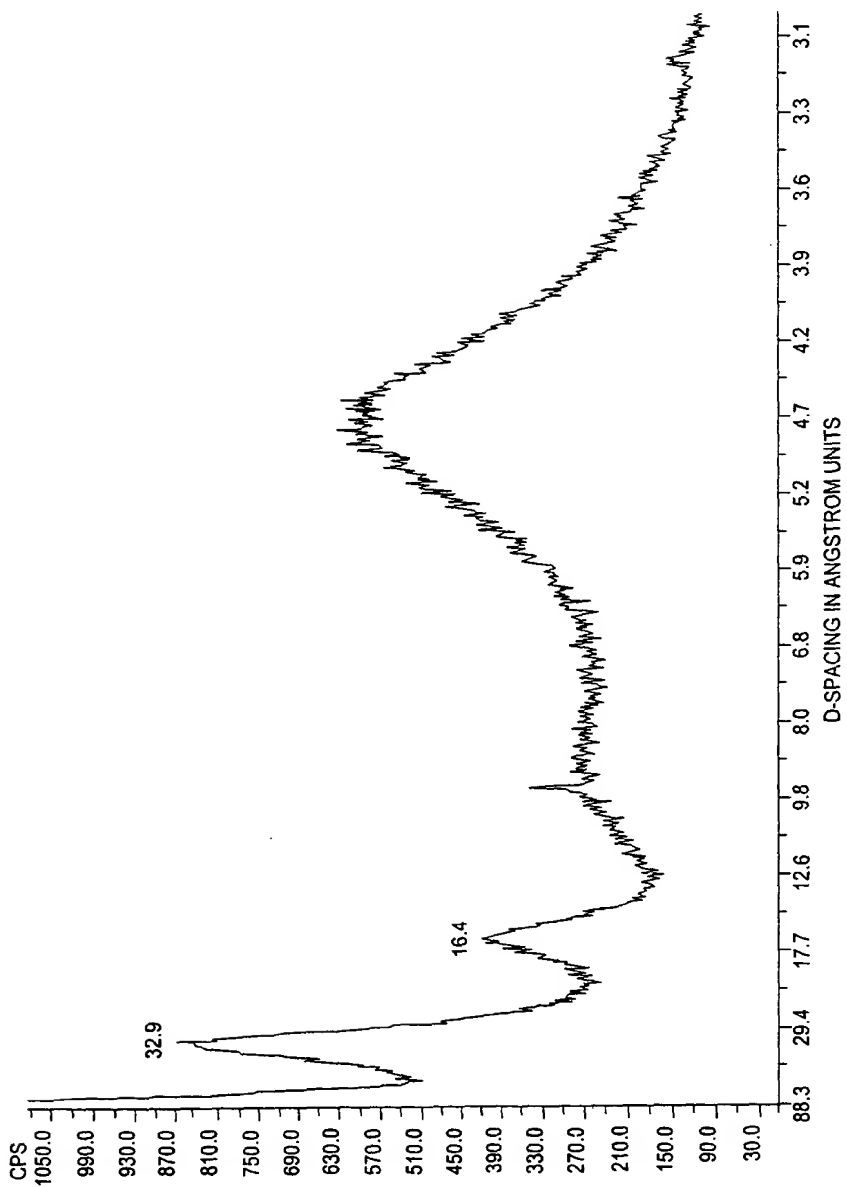
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FIG. 6



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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/29133

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B33/44 C08K9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 798 267 A (RHEOX INTERNATIONAL, INC.) 1 October 1997 (1997-10-01)	1,10-12, 14, 20-29, 31,41-43
Y	the whole document	2,4-9, 13,15-19 30,32,33
A	---	
Y	WO 97 42279 A (AKZO NOBEL NV) 13 November 1997 (1997-11-13) claims 9-30,32,33 page 7, line 1 -page 11, line 6 ---	2,4-9, 13,15-19
	--- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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